STRUCTURAL AND ELECTROCHEMICAL CHARACTERISITICS OF LAYERED MANGANESE BRONZE SYNTHESIZED USING A SOL-GEL METHOD

K. S. Park, M.H. Cho, S. H. Park [a], Y. K. Sun[a], K. S. Nahm*, Y. S. Lee[b], M. Yoshio[b] ,

School of Chemical Engineering and Technology,

College of Engineering,

Chonbuk National University, Chonju 561-756, Korea

[a] Department of Industrial Chemistry, College of Engineering, Hanyang

University, Seoul 133-791, Korea

[b] Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840-8502, Japan

Abstract

Recently proposed layered Li-Mn oxide-based materials ($Li_{2/3}[Ni_xMn_{1-x}]O_2$, x =1/6 ~ 1/3) have shown promising properties as a positive electrode active material for lithium secondary batteries due to their low cost, large theoretical capacity, and environmental safety. In this work, O_2-$Li_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ was prepared by ion exchange of Li for Na from precursor P2-$Na_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ synthesized by a sol-gel method as functions of chelating agent and calcination temperature. In order to clearly understand the influence of the temperature on the synthesis of O2-$Li_{2/3}[Li_{1/6}Mn_{5/6}]O_2$, P2-$Na_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ precursor was synthesized in the calcinations temperature range of 700 ~ 1000℃ using glycolic and adipic acids as chelating agent, respectively. The effect of Ni doping in the synthesized material was investigated to increase the discharge capacity and suppress the capacity fading.

Powder X-ray diffraction (XRD) was used to characterize the purity and structure of the prepared samples. Ion exchange in hexanol was almost completed for Li ion with 1/6 and the samples had O2 structure with faults. The structural and electrochemical characteristics of $Li_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ prepared at 800 ℃for 10 h using glycolic acid were better than those prepared using adipic acid. Figure 1 show that Ni doped $Li_{2/3}[Ni_{1/6}Mn_{5/6}]O_2$ observed almost the same properties as that prepared at 800℃for 10 h using glycolic acid. But it was found that the Ni doped sample included T2 structure.

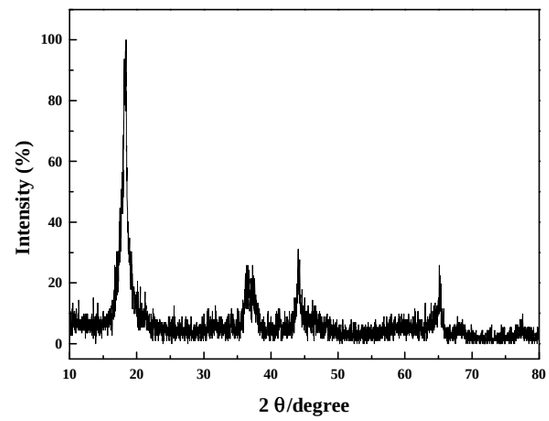
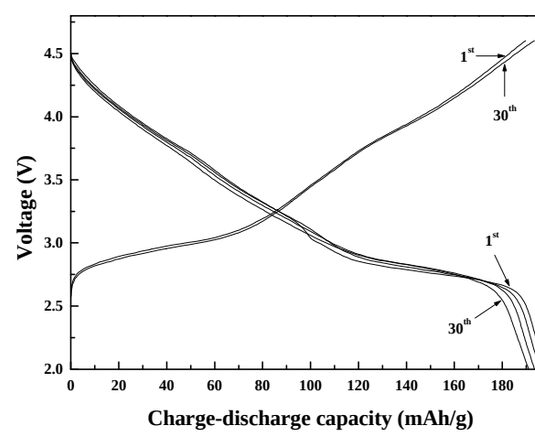


Fig. 1. XRD pattern of Ni-doped $Li_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ powders prepared at 800 ℃ using glycolic acid

The electrochemical test was performed using CR2032 coin-type cells fabricated with the samples prepared for 10 h at 800 ℃ using adipic acid (sample B) and glycolic acid (sample F) as chelating agent. The sample B delivered the initial discharge capacity of 145 mAh/g, but the capacity decreased to be 125 mAh/g after 30th cycle, which corresponds to the capacity fading rate of 0.49%. Meanwhile, the discharge capacities of the sample F at the 1st and 30th cycles were 187 and 169 mAh/g, respectively. The capacity fading rate was 0.42 % per a cycle. The discharge capacity of Ni-doped O2-$Li_{2/3}[Ni_{1/6}Mn_{5/6}]O_2$ delivered 198 mAh/g at the first cycle with the capacity retention rate of 97% after 30 cycles. The discharge capacity of Ni doped-$Li_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ increased and the capacity retention rate was significantly improved. The merits of cation doping in O2 structure has been intensively discussed in this work



Charge-discharge curves of Li cell containing $Li_{2/3}[Ni_{1/6}Mn_{5/6}]O_2$ prepared at 800 ℃ using glycolic acid